DIFFUSION OF OXYGEN INTO PITCH FIBERS

L.S. Singer, Consultant
525 Race Street
Berea, OH 44017

S. Mitchell
Amoco Performance Products, Inc.
4500 McGinnis Ferry Road
Alpharetta, GA 30202

Introduction

The physical diffusion of molecular oxygen into pitch is the first step in the cross-linking and polymerization processes which lead to infusibilization (thermosetting) of pitch by air or oxygen. An early study of both the experimental and theoretical aspects of thermosetting was carried out by Stevens and Diefendorf [1]. More recently, Cornec et al. demonstrated the importance of the sorption-diffusion step in the stabilization process [2]. In this paper, we have shown that it is possible to measure by electron paramagnetic resonance (EPR) techniques, physical diffusion rates of molecular oxygen into pitch; and to interpret the results using a dimensionless mathematical model similar to that proposed earlier [1].

The method derives from the fact that paramagnetic oxygen significantly affects the EPR relaxation times of the naturally-occurring stable free radicals in pitch [3]. At temperatures below those required for chemical reaction, the effect is purely physical and is truly reversible. Thus, for the diffusion of molecular oxygen into pitch, the diffusion coefficient and its temperature dependence can be determined by relating the rate of modification of electron spin relaxation in pitch fibers to a mathematical model.

Experimental Concepts and Results

These relaxation and diffusion phenomena can be illustrated by utilizing as-spun pitch fibers of a variety of diameters. For example, 11 μm diameter as-spun mesophase pitch fibers exhibited the room-temperature EPR saturation behavior shown in Fig. 1. All fibers from a given pitch (diameters between 11 μm and 3 mm) exhibited essentially the same saturation behavior after 24 hours of evacuation at room temperature. This behavior would be expected for pitch preparation and spinning under oxygen-free conditions.

The diffusion experiments consist of measuring, at a constant microwave power level, the rate of conversion of the bottom curve to the top curve in Fig. 1, when air is suddenly admitted to the evacuated sample. That is to say, the ratio of the O_2 concentration within the fiber at time (t) to that at infinite time (solubility of oxygen in pitch at a given ambient oxygen pressure) will be given by the ratio of the corresponding changes in EPR signals, as shown in the inset block in Fig. 1.

The room-temperature EPR diffusion results for several mesophase pitch fibers of different diameters are shown in Fig. 2. An isotropic pitch fiber and several partially and totally thermoset fibers exhibited essentially the same oxygen diffusion rates as the as-spun mesophase pitch fibers.

A dimensionless mathematical model for thermosetting fibers was derived and simplified for the pure diffusion case. The model generated the curve shown in Fig. 3, of normalized free oxygen content of the fiber versus dimensionless time. Using the diffusion rates measured by EPR, the diffusion coefficients were then evaluated. The value $D = 2 \times 10^{-9}$ cm²/sec obtained for room temperature is comparable to that observed for other molecular sieve materials such as zeolites and coals [4]. The D-values determined were essentially independent of fiber diameter.

The temperature dependence of the diffusion coefficients calculated from the model using the EPR diffusion rates, is shown in the activation energy plot in Fig. 4. The activation energy $\Delta E = 8.0$ kcal/mole is consistent with literature values for activated diffusion [4]. From the diffusion coefficients and the curve in Fig. 3, the times for 50% and 90% completion of the diffusion process were calculated for mesophase pitch fibers of several diameters and the results are given in Table I.

TABLE I
Diffusion Times ($t_{.5}$ and $t_{.9}$) Required for Mesophase Pitch Fibers to Attain 50% and 90% of their Oxygen Sorption Capacity

r_s (μm)	T(°C)	D(cm²/sec)	$t_{.5}$	$t_{.9}$
10	25	1.9×10^{-9}	36 sec	190 sec
100	"	"	60 min	313 min
1000	"	"	100 hrs	522 hrs
10	100	3.2×10^{-8}	2.1 sec	11 sec
100	"	"	3.5 min	18 min
1000	"	"	5.8 hrs	30 hrs
10	150	1.3×10^{-7}	.52 sec	2.7 sec
100	"	"	.87 min	4.5 min
1000	"	"	1.5 hrs	7.8 hrs

The predictions in Table I are consistent with R.T. Lewis's conclusions [5] that for small-diameter fibers the oxygen diffusion is quite rapid, so that the thermosetting process is reaction-controlled rather than diffusion-controlled. The diffusion results for the larger-diameter pitch rods suggest that the limited depth of high-temperature thermosetting reported for pitches may be due to the inhibition of oxygen diffusion by reaction products.

It should be pointed out that these EPR measurements and their analysis cannot determine the maximum equilibrium oxygen concentration (solubility) for a given pitch. To fully analyze thermosetting situations, both diffusion and solubility measurements as a function of temperature and oxygen pressure would be required.

Conclusions:

1. The diffusion coefficients for the diffusion of molecular oxygen into pitch can be determined by interpreting the EPR relaxation behavior of the free radicals in pitch with a dimensionless mathematical model.
2. The diffusion coefficients and their temperature dependence are comparable to other molecular sieve materials [4].
3. The results are consistent with the findings [5] that for small diameter fibers, the thermosetting process is reaction-controlled rather than diffusion-controlled.
4. The diffusion results on thermoset fibers offer no evidence for the existence of the impermeable skins or diffusion barriers which have been suggested [2,6].
5. The limited depth of high-temperature oxidative thermosetting in pitch may be due to the inhibition of oxygen diffusion by reaction products.

Acknowledgments

The authors wish to thank D.T. Orient and D.M. Riffle for their assistance with the EPR measurements and Dr. R.T. Lewis for several useful discussions.

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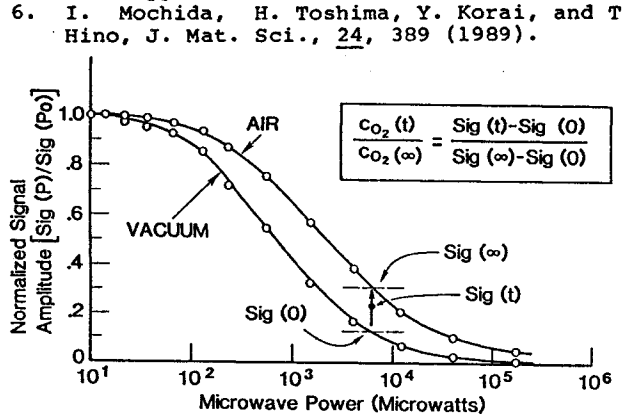

Fig. 1. EPR saturation curves for 11 μm diameter mesophase pitch fibers.

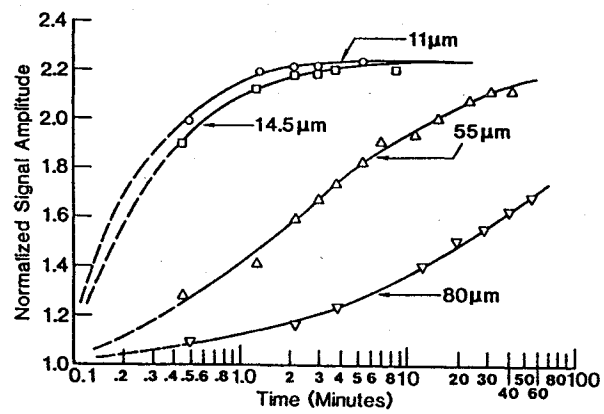

Fig. 2. EPR signal vs. time for mesophase pitch fibers of different diameters, 25°C.

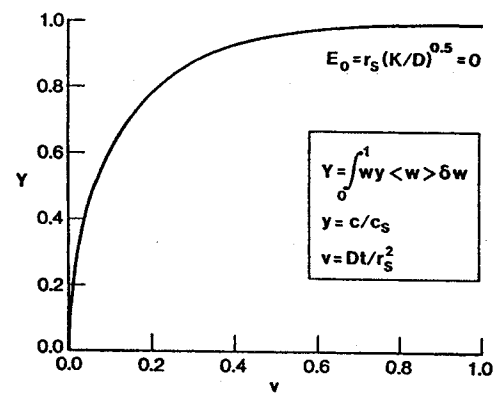

Fig. 3. Normalized free oxygen content of the fiber, Y, vs. the dimensionless time v. The symbols K and $w=r/r_s$ are the reaction rate constant and the dimensionless fiber radius, respectively.

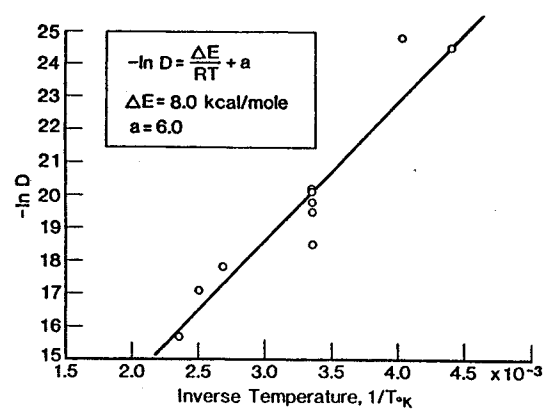

Fig. 4. Activation energy for O_2 diffusion into mesophase pitch; least squares plot.